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RAPID AND SENSITIVE SPECTROPHOTOMETRIC DETERMINATION OF CERIUM(IV) WITH 2,4-DIHYDROXY BENZOPHENONE BENZOIC HYDRAZONE

C. Kesava Rao, V. Krishna Reddy and T. Sreenivasulu Reddy
Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 003, India

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Summary—A simple and sensitive spectrophotometric method for the determination of cerium(IV) in an aqueous medium is reported. The metal ion formed a 1:1 orange–red coloured complex with 2,4-dihydroxy benzophenone benzoic hydrazone (DHBPBH) at pH 10.0 showing an absorption maximum at 400 nm. The molar absorptivity and Sandell's sensitivity of the method are found to be 2.0×10^4 l/mol/cm and 0.007 $\mu g/cm^2$, respectively. Beer's law is obeyed in the range 0.7–7.0 $\mu g/ml$. Titanium, vanadium and molybdenum do not interfere. The extent of interferences by other ions is presented. The method is applied for the determination of cerium in simulated rock samples.

Rare earth element geochemistry has been established as one of the most powerful tools for petrogenetic studies of rocks. The spectrophotometric studies of cerium are usually carried out with organic dye stuffs.[1,2] Most of these methods suffer from serious interference of many ions like thorium, uranium, titanium, zirconium, iron, nickel and fluoride. Among the most recently reported methods,[3–10] though some of them are highly sensitive, either they suffer from the interference of other rare-earth metal ions or involve an extraction procedure.

2,4-Dihydroxy benzophenone benzoic hydrazone (DHBPBH) forms an intense orange–red coloured solution with cerium(IV) in alkaline medium (pH 8–11). The coloured solution is quite stable and its absorbance varies proportionately with micro amounts of cerium(IV). Hence a systematic study has been made to develop a sensitive direct spectrophotometric method for the determination of micro amounts of cerium.

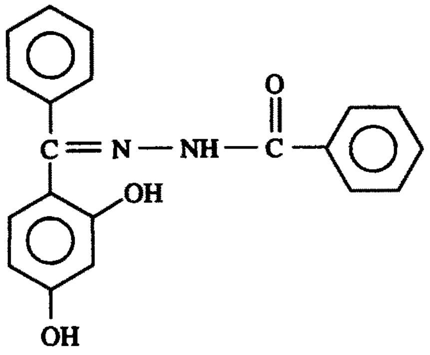
EXPERIMENTAL

Reagents

Stock solution of ammonium ceric sulphate (0.1*M*) was prepared by dissolving the requisite amount of AnalaR grade (BDH) sample. The solution was standardized volumetrically.[11] The lower concentrations were prepared by appropriate dilution of the stock solution.

2,4-Dihydroxy benzophenone benzoic hydrazone

The reagent was prepared by condensing 2,4-dihydroxy benzophenone and benzoic hydrazide in ethanol medium using the general procedure[12] (m.p. 274–276°C). The reagent has the following structure.



A 0.01*M* solution in dimethylformamide is used in the studies.

Buffer solutions

Ammonium hydroxide (2.0*M*) and ammonium chloride (2.0*M*) were used for the preparation of buffer solutions.

Apparatus

A Shimadzu UV–visible spectrophotometer model UV-160A equipped with 1 cm quartz cells and Philips Digital pH meter model PP 9046 were used for absorbance and pH measurements, respectively.

Recommended procedure

In each of a set of different 10 ml volumetric flasks, 5 ml of buffer solution (pH 10.0), various volumes of $1 \times 10^{-3} M$ metal solution, 2 ml of $(1 \times 10^{-2} M)$ DHBPBH and 1 ml of dimethylformamide were added. The contents were made up to the mark with distilled water. The absorbance was measured at 400 nm against reagent blank. A linear plot passing through the origin was obtained when absorbance was plotted against the amount of cerium. The calibration graph follows the equation

$$Y = mx + b$$

where x is concentration of the solution, Y is measured absorbance and m and b are constants. The correlation coefficient (γ) of this equation for the experimental data is obtained as 0.990.

RESULTS AND DISCUSSION

Spectral characteristics

The absorption spectra of the reagent and the complex were recorded in the wavelength range 350–460 nm at pH 10.0 against the buffer solution and reagent blank, respectively. The complex shows an absorption maximum at 400–405 nm (Fig. 1). Hence further studies were carried out at 400 nm.

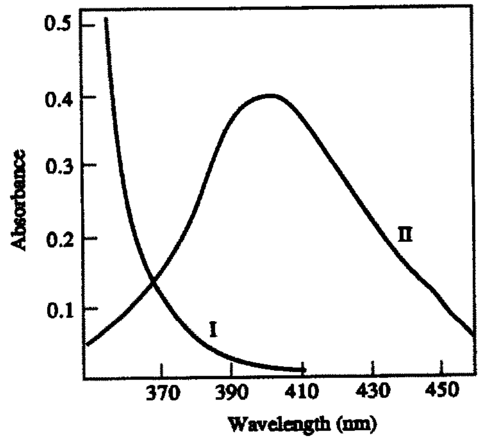


Fig. 1. (1) Reagent spectrum (DHBPBH). (2) Metal complex spectrum [DHBPBH + Cerium(IV)]. [DHBPBH] = $4.0 \times 10^{-4} M$; [Cerium(IV)] = $2.0 \times 10^{-5} M$.

It was observed that the composition and colour intensity of the complex vary with pH. By employing Vosburgh and Cooper's method,[13] the absorption spectra of the reaction mixture at different pH values were recorded and presented in Fig. 2. The figure indicates the absorption maximum at 390 nm (pH 8.0), 410 nm (pH 8.5), 490 nm (pH 9.0), 430 nm (pH 9.5), 400 nm (pH 10.0) and 390 nm (pH 10.5) with variable metal to ligand composition. This indicates the formation of different soluble complex species at different pH values.

Stoichiometry of the complex species

The stoichiometry of different complex species formed at different pH values were determined by employing molar ratio method.[14] The results are presented in Table 1. A similar behaviour was observed by Vallvey *et al.*[15] in the determination of titanium. Cartagena *et al.*[4] observed the formation of two different complex species between cerium(IV) and methyl thymol

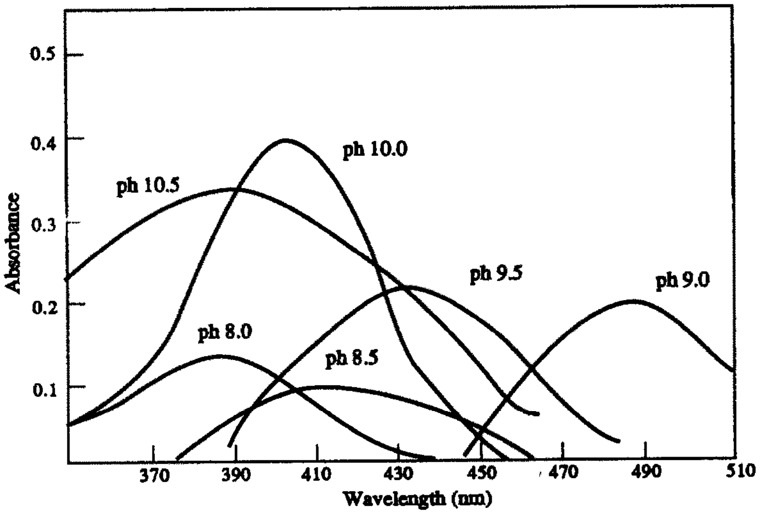


Fig. 2. Metal complex spectra [DHBPBH + Cerium(IV)] at various pH values (pH 8.0–10.5). [DHBPBH] = $4.0 \times 10^{-4} M$; [Cerium(IV)] = $2.0 \times 10^{-5} M$.

Table 1. Stoichiometries of Ce(IV)-DHBPBH complexes

pH	Composition (*Metal*:*Ligand*)	λ_{max} (*nm*)	Molar absorptivity ($\times 10^4$ *l/mol/cm*)
8.0	2:3	390	0.65
8.5	1:1	410	0.50
9.0	1:2	490	1.00
9.5	2:3	430	1.10
10.0	1:1	400	2.00
10.5	1:2	390	1.65

blue depending on the order of addition of the reactants. The molar absorptivity was found to be highest at pH 10.0. Hence the analytical studies were carried out for the complex species formed at pH 10.0.

Spectrophotometric determination of cerium(IV)

Effect of reagent. The absorbance of the complex species was studied as a function of molar ratio of DHBPBH to cerium(IV) at pH 10.0. A 20-fold molar excess of the reagent over cerium(IV) was necessary to obtain maximum

Table 2. Tolerance limit of diverse ions in the determination of cerium(IV). Amount of cerium(IV) taken = 2.00 μg/ml

Diverse ion	Tolerance limit (*μg/ml*)	Diverse ion	Tolerance limit (*μg/ml*)
EDTA	1300	Zn(II)	760
Thiosulphate	480	Cd(II)	689
Oxalate	360	U(VI)	600
Tartrate	286	Ni(II)	600
Thiocyanate	200	Co(II)	580
Iodide	135	Fe(III)	200,500*
Nitrate	130	W(VI)	100
Fluoride	130	Th(IV)	100
Carbonate	100	La(III)	100
Thiourea	90	Gd(III)	110
Phosphate	70	Nd(III)	100
Ascorbic acid	70	Sm(III)	86
		Yb(III)	86
		Zr(IV)	86
		Cr(VI)	68
		Cu(II)	20,68*
		Pd(II)	56
		Ag(I)	38
		Mg(II)	28
		Pt(IV)	18
		Hg(II)	8

*In presence of 1200 μg of EDTA.

Table 3. Analysis of synthetic mixtures of rock samples

Sample (% of composition)	Amount of cerium (*μg/ml*)			% of error between taken value and present method	Standard deviation
	Taken	Found AAS method	Found Present* method		
GS-N (Granite)					
SiO_2: 65.80; Al_2O_3: 14.67; Fe_2O_3: 1.92	1.24	1.22	1.20	−3.22	0.014
FeO: 1.65; MnO: 0.056; MgO: 2.30; CaO: 2.50;	2.43	2.40	2.46	1.23	0.010
Na_2O: 3.77; K_2O: 4.63; TiO_2: 0.68; P_2O_5: 0.28;	6.10	6.09	6.06	−0.65	0.016
La: 0.075; Ce: 0.135; Nd: 0.050; Eu: 0.0017;					
Dy: 0.003; Yb: 0.0015; Sm: 0.0077; Gd: 0.0052;					
Er: 0.0017; Lu: 0.0022; Y: 0.019					
QLO-1 (Quartzlatite)					
SiO_2: 65.55; Al_2O_3: 16.18; Fe_2O_3: 1.02;	0.90	0.89	0.88	−2.22	0.017
FeO: 2.97; MnO: 0.093; MgO: 1.00, CaO: 3.17;	1.70	1.68	1.69	=0.58	0.018
Na_2O: 4.20; K_2O: 3.60; TiO_2: 0.624; P_2O_5: 0.254;	2.02	2.00	2.06	1.98	0.012
La: 0.027; Ce: 0.0546; Nd: 0.026; Eu: 0.00143;					
Dy: 0.0033; Yb: 0.00232; Sm: 0.00488;					
Gd: 0.0047; Er: 0.0023; Lu: 0.00037;					
Y: 0.024.					
BE.N (Basalt)					
SiO_2: 38.20; Al_2O_3: 10.07; Fe_2O_3: 5.34;	0.88	0.90	0.86	−2.27	0.014
Feo: 6.74; MnO: 0.20; MgO: 13.15; CaO: 13.87;	2.02	2.00	2.06	1.98	0.020
Na_2O: 3.18; K_2O: 1.39; TiO_2: 2.61; P_2O_5: 1.05;	3.80	3.79	3.76	−1.05	0.016
La: 0.082; Ce: 0.152; Nd: 0.070; Eu: 0.0036;					
Dy: 0.0064; Yb: 0.0018; Sm: 0.012; Gd: 0.0095;					
Er: 0.0025; Lu: 0.00024; Y: 0.030					
SDC-1 (Mica Schist)					
SiO_2: 65.85; Al_2O_3: 15.75; Fe_2O_3: 2.62;	1.30	1.29	1.33	2.30	0.020
FeO: 3.93; MnO: 0.114; MgO: 1.69; CaO: 1.40;	2.55	2.58	2.48	−3.12	0.016
Na_2O: 2.05; K_2O: 3.28; TiO_2: 1.01; P_2O_5: 0.158;	6.30	6.29	6.28	−0.31	0.012
La: 0.042; Ce: 0.093; Nd: 0.040 Eu: 0.00171;					
Dy: 0.0067; Yb: 0.004; Sm: 0.0082; Gd: 0.0072;					
Er: 0.004; Lu: 0.00053; Y: 0.040.					

*Average of six determinations.

absorbance at 400 nm. Presence of excess of reagent does not affect the absorbance values.

Stability of the complex. The orange–red colour development was complete in 10 min after mixing of the reactants. The complex was stable for more than 24 hr.

Beer's law is obeyed between 0.7 and 7.0 μg/ml of cerium. The molar absorptivity is 2.0×10^4 l/mol/cm and Sandell's sensitivity is found to be 0.007 μg/cm^2. The relative standard deviation of the method in the determination of 2.0 μg of cerium is found to be 0.26 ppt (2.6%).

Interference studies. The recommended procedure was used to determine cerium(IV) in presence of potential interfering ions. To a solution containing 2 μg of cerium, 1 ml of ($4 \times 10^{-3}M$) DHBPBH, 5 ml of buffer solution (pH 10.0), varying amounts of diverse ions were added and the absorbance was measured. The tolerance limit for foreign ions was taken as the amount that caused an error in the absorbance value by ±2%. Titanium(IV), vanadium(V) and molybdenum(VI) do not interfere in any concentration level. The tolerance limit of other ions is presented in Table 2.

Application of the method for rock samples. It is shown[16] that the rock samples namely Granite (GS-N), Quartz latite (QLO-1), Mica schist (SDC-1) and Basalt (BE-N) possess a sufficient concentration of cerium. Since the original rock samples were not available, simulated samples containing all the components in the same proportions, as present in the original rock samples, were prepared by mixing the pure salts of these components. Then cerium present in these mixtures was determined by the present method.

Known aliquots of sample solutions were transferred into a 10 ml volumetric flask containing 5 ml of buffer solution, 2 ml of ($1 \times 10^{-2}M$) reagent and 1 ml of dimethylformamide. The contents were made up to the mark with distilled water. The absorbance of the solutions was measured at 400 nm against the reagent blank. The amounts of cerium present in the samples were computed from the predetermined calibration plot.

The amounts of cerium obtained by the present method are compared against those obtained by AAS method. The results obtained are presented in Table 3.

Comparison of the results

The results obtained in the present method are compared with those obtained by other methods. The sensitivity of the formaldoxime method ($\epsilon = 3.2 \times 10^3$)[17] and oxine method ($\epsilon = 6.7 \times 10^3$)[18] is much less than that of the present method. The sensitivity of methyl

Table 4. Comparison of spectrophotometric methods for the determination of cerium(IV) with various chromogenic reagents

Reagent	ϵ (*l/mole/cm*)	λ_{max} (*nm*)	pH	Composition (*M*:*L*)	Beer's law range (*μg/ml*)	Interference	Ref.
Methyl thymol blue	1.0×10^4	540	6.5	1:1	0.5–7.0	—	4
Methyl thymol blue	2.7×10^4	625	10.2	1:2	0.09–3.4	Cu(II), Mg(II), Ca(II), Sr(II), Ba(II), Cd(II) Hg(I), Al(II), Zr(IV), Th(IV), Pb(II), Bi(II), Cr(III), V(VI), Mn(II), Fe(II), Fe(III), PO_4^{3-} interfered.	8
Pyrogallol red	9.2×10^3	640	5.2	1:1	0.84–10.08	—	10
Pyrogallol red (Indirect method)	—	507	5.0	2:1	0–15	Ti(IV), Al(II), Fe(III), Th(IV), Mo(VI), W(VI), Cu(II), Cr(VI), Sb(V), V(V) Zr(IV) interfered.	9
o-Iodobenzoyl-*o*-tolylhydroxylamine	5.744×10^2	450	Ammonical medium	1:4	0.4–32	—	7
N-*p*-chlorophenyl-2-furylacrylohydroxyamic acid with or without 1-(2-pyridylazo)-2-naphthol	8.5×10^3 1.8×10^4	470 515	Acidic medium	—	—	—	6
2,4-Dihydroxybenzophenone benzoichydrazone	2.0×10^4	400	10.0	1:1	0.3–7.0	Cu(II)	Present method

thymol blue method[8] is higher than that of the present method. But it is less stable (25 min) and suffers from the interference of many cations. Comparison with some of the recently proposed methods is also made and presented in Table 4.

CONCLUSIONS

In the present paper a sensitive and selective spectrophotometric method for the determination of cerium(IV) is reported. The metal ion reacts with 2,4-dihydroxy benzophenone benzoic hydrazone (DHBPBH) in ammonical buffer medium to give an orange–red coloured complex. The coloured solution shows absorption maximum at 400 nm at pH 10.0. The method avoids the interference of most of the ions which are normally found along with cerium in natural samples.

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